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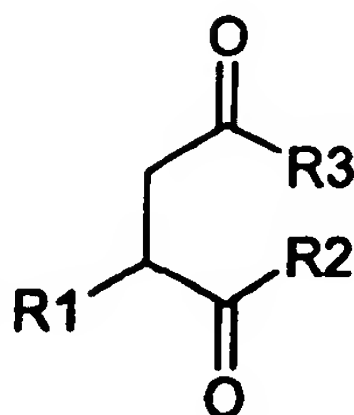
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(54) Title: FUEL ADDITIVES



(I)

(57) Abstract: A method of increasing the lubricity of a liquid hydrocarbon fuel comprising the addition of one or more compounds of formula (I) where R<sub>1</sub> is a C<sub>10</sub>-C<sub>150</sub> alkenyl group, one of R<sub>2</sub> and R<sub>3</sub> is -OH or the residue of a C<sub>1-20</sub> monohydroxy alcohol and the other of R<sub>2</sub> and R<sub>3</sub> is -OH or the residue of either a C<sub>1-20</sub> monohydroxy alcohol or a C<sub>1-20</sub> polyhydroxy alcohol, with the proviso that R<sub>2</sub> and R<sub>3</sub> are not both -OH.

### Fuel additives

This invention relates to fuel additives, more particularly to additives which increase the lubricity of the fuel and avoid both undesirable interactions with the other additives now commonly present in fuels and cross-contamination between different fuel types in the distribution system.

It is known to add a minor proportion of a long chain fatty acid to liquid hydrocarbon fuels to increase the lubricity of the fuel, that is the ability to prevent wear on contacting metal surfaces. Increased lubricity results in lower wear to the surface, as measured for example by the well known wear scar test described in more detail hereinafter. Fatty acids which have been used for this purpose include di-linoleic acid. However, the increasing number of additives now present in fuels, and increased dosing levels, means that a need is arising for lubricity additives with an inherently lower tendency to interact with other fuel and lubricant additives. Improved lubricity performance for such compounds, relative to known lubricity additives, would also be desirable.

Esters of fatty acids have also been proposed as lubricity additives. Whilst the acid functions of these molecules are blocked by an alkyl ester group and so are not available for interaction with other fuel additives, it is important that the performance of the lubricity additive is not reduced by esterification, so that a delicate balance of properties is required.

WO97/44507 discloses *bis*-esters of alkenyl succinic acids with ethylene glycol, propylene glycol, glycerol and polyoxyalkylenes. The succinic acids have 10-32 carbon atoms in the alkenyl chain.

Certain of the prior art cited in WO97/44507 is also relevant:

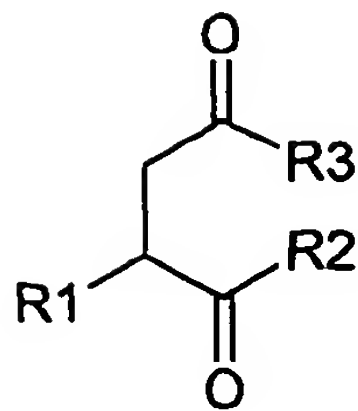
US-A-4448586 (Weidig) discloses liquid fuels having anti-corrosion properties for use in internal combustion engines. The corrosion inhibition is discussed in relation to alkanol-type fuels and the reactant ratios are such that  $\text{RCOO} \cdot \text{CH}_2\text{CH}_2 \cdot \text{OOCR}$  structures are present.

US-A-5080817 (Meyer) also discloses corrosion inhibitor compositions in which the reactant ratios are such that  $\text{RCOO} \cdot \text{CH}_2\text{CH}_2 \cdot \text{OOCR}$  structures are present.

US-A-2993773 (Stromberg) discloses deposit modifiers for use in gasolines and jet fuels. One such deposit modifier is a *bis*-ester of an alkenyl succinic acids with ethylene glycol wherein the succinic acid have 12 carbon atoms in the alkenyl chain.

We have now discovered a class of esterified alkenyl succinic acids which, while demonstrating excellent performance as lubricity additives, also offer improved compatibilities with other fuel and lubricant additives and reduced carryover between fuels in the distribution system, for example fuel pipelines, tankers, etc., as measured by their improved water separation characteristics.

The compounds are represented by the general formula (I)



(I)

where  $R_1$  is a  $C_{10}$ - $C_{150}$  alkenyl group, such as an olefin or polyolefin, one of  $R_2$  and  $R_3$  is -OH or the residue of a  $C_{1-20}$  monohydroxy alcohol and the other of  $R_2$  and  $R_3$  is -OH or the residue of either a  $C_{1-20}$  monohydroxy alcohol or a  $C_{1-20}$  polyhydroxy alcohol, with the proviso that  $R_2$  and  $R_3$  are not both -OH.

$R_1$  is preferably a  $C_{16}$ - $C_{80}$  group and more preferably a polyisobutene (PIB). The molecular weight of the PIB is preferably 200-2000, more preferably 260-1000, for example about 260, 320, 350, 550, 750 or 1000. Conventional PIBs and so-called "high-reactivity" PIBs (see for example EP-B-0 565 285) are suitable for use in the invention. High reactivity in this context is defined as a PIB wherein at least 50%, preferably 70% or more, of the terminal olefinic double bonds are of the vinylidene type, for example the GLISSOPAL compounds available from BASF.

$R_2$  and  $R_3$  are -OH or the residues of alcohols, although  $R_2$  and  $R_3$  are not both simultaneously -OH, i.e. the compound is always at least semi-esterified. Partial esters of another type are also envisaged, i.e. compounds in which one carboxyl group is fully esterified and one carboxyl group is only partially esterified. In other words the invention encompasses mixtures of the fully and semi-esterified compounds in a variety of ratios. A good measure of the degree of esterification under these circumstances is given by the acid number, i.e. the amount of NaOH required to neutralise 1 g of the compound. This is generally less than 90 mg NaOH/g, corresponding approximately to

semi-esterification (although it is also dependent on molecular weight), preferably less than 50 mg NaOH/g, for example less than 20 mg NaOH/g, less than 10 mg NaOH/g or less than 5 mg NaOH/g.

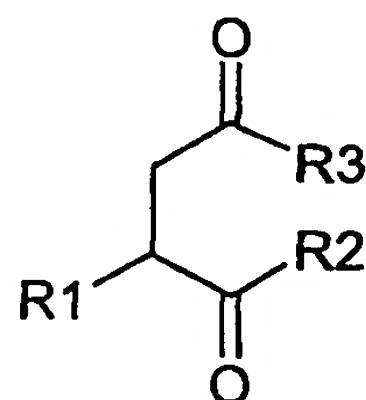
The  $R_2$  and  $R_3$  alcohols can be either be mono- or polyhydroxy alcohols, i.e. alcohols having one, two or more hydroxy groups, in the case of polyhydroxy alcohols one of which esterifies the carboxylic acid moiety of the succinic acid. One or both of the groups  $R_2$  and  $R_3$  is derived from a monohydroxy alcohol. The monohydroxy alcohols are preferably  $HO-R_4$  where  $R_4$  is a  $C_{1-20}$  straight or branched chain hydrocarbon.  $R_2$  and/or  $R_3$  preferably are methanol, ethanol, propanol or isopropanol. When only one of  $R_2$  and  $R_3$  is a monohydroxy alcohol the other is preferably  $\{OCH_2CH_2\}_nOH$ ,  $\{OCH_2CHCH_3\}_nOH$  or  $-OCH_2CHOHCH_2OH$  with  $n = 1-10$  and more preferably ethylene glycol or glycerol, i.e.  $n = 1$ , or diethylene glycol, i.e.  $n = 2$ . Also useful are higher sugars, i.e. longer chain analogues of glycerol of formula  $-OCH_2\{CHOH\}_nCH_2OH$  with  $n = 2-4$ .

The compounds of formula (I) may be added to middle distillate fuels of poor lubricity, such as those with poor inherent lubricity, and those which have been exposed to hydrotreatment or desulphurisation processes thereby lowering the sulphur concentration to 0.5% w/w or less, e.g. 0.2 % w/w, 0.05 % w/w or lower, for example diesel fuels (typical distillation range 150-400 °C) and heating oils (typical distillation range 150-450 °C), and also to gasolines (typical distillation range 30-210 °C), kerosines (typical distillation range 140-300 °C) and heavy fuel oils (typical distillation range 300-600 °C). An aspect of the invention thus comprises methods of increasing the lubricity of such fuels by addition of the compounds of the invention.

Compounds of formula (I) may be dosed in amounts between 5 and 5000 ppm, preferably between 10 and 500 ppm and most preferably between 30 and 300 ppm, to improve the lubricity properties of the fuels.

It is particularly advantageous to add a compound of formula (I) to the fuel in combination with one or more of the known compounds of WO97/44507, hereinafter referred to as a compound of formula (Ia).

Thus the invention also provides methods of increasing the lubricity of the abovementioned fuels comprising the addition of one or more compounds of formula (I) and one or more compounds of formula (Ia)



(Ia)

where  $R_1$  is a  $C_{10}$ - $C_{32}$  alkenyl group, such as an olefin or polyolefin,  $R_2$  and  $R_3$  are  $(OCH_2CH_2)_nOH$ ,  $(OCH_2CHCH_3)_nOH$  or  $-OCH_2CHOHCH_2OH$  with  $n = 1-10$ , and wherein the compound of formula (I) and the compound of formula (Ia) may be added separately or in combination.

$R_1$  in formula (Ia) is most preferably a  $C_{12}$ - $C_{26}$  group. The value of  $n$  in these compounds is most preferably 1 or 2, and in particular  $R_2$  and  $R_3$  can be ethylene glycol.

The total dosages of the compounds of formula (I) and formula (Ia), when added to a fuel to give a combined lubricity enhancement, are conveniently between 5 and 5000 ppm, preferably between 10 and 500



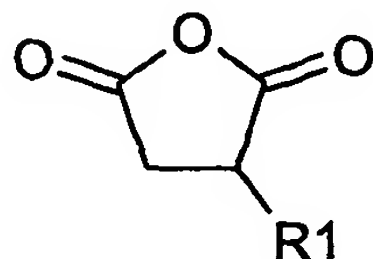
ppm and most preferably between 30 and 300 ppm. Suitably the ratio of the compounds of formula (I) and formula (Ia) is between 10:90 and 90:10 parts by weight, most conveniently between 50:50 and 90:10 parts by weight, i.e. with the compound of formula (I) predominating.

Diesel fuels and heating oils will typically contain less than 0.2% w/w sulphur and may contain, in addition to the additive compositions of this invention, any of the other additives commonly added as minor components, such as cetane improvers, cold flow improvers, detergent/dispersant additives, antifoam additives, dehazing additives, combustion improvers, antioxidants, etc.

As used herein, "gasoline" refers to motor fuels meeting ASTM standard D-439, and includes blends of distillate hydrocarbon fuels with oxygenated components, such as MTBE, ETBE, ethanol, etc. as well as the distillate fuels themselves. The fuels may be leaded or unleaded, and may contain, in addition to the additive compositions of this invention, any of the other additives conventionally added to gasolines, such as scavengers, anti-icing additives, octane requirement improvers, detergent packages, antioxidants, demulsifiers, corrosion inhibitors, etc.

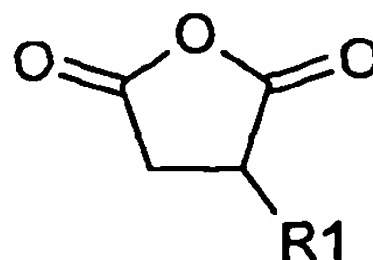
The invention also provides fuel additive compositions suitable for use in any of the previous aspects of the invention, the compositions comprising one or more compounds of formula (I) and one or more compounds of formula (Ia), in a fuel-miscible solvent, for example toluene, xylene, Shellsol (available from Shell) or an environmentally friendly solvent such as the low aromatic solvent Finalan (available from Fina), and furthermore optionally containing other ingredients conventionally used in fuel additive packages.

The compounds of formula (I) may for example be prepared by reacting an anhydride of formula



with an alcohol of formula  $R_2OH$  and/or  $R_3OH$  where  $R_2$  and  $R_3$  are as defined above. For semi-esterification as referred to, above, only one of  $R_2OH$  and  $R_3OH$  need be reacted. For partial esterification of one or other carboxyl group, the reaction with  $R_2OH$  or  $R_3OH$  need not be taken to completion. Under appropriate reaction conditions it is possible to prepare in a one-pot synthesis a blend of a compound of formula (I) and a compound of formula (Ia), for example when a first esterification is carried out with a monohydroxy alcohol and then a second esterification with an excess of a polyhydroxy alcohol. The polyhydroxy alcohol can effect a degree of transesterification, displacing the monohydroxy alcohol as well as esterifying the second (free) carboxyl group.

The starting anhydride of formula



is conveniently prepared by addition of the olefin or polyolefin across the double bond of maleic anhydride by processes known per se.



The invention is illustrated by the following examples.

Preparation of compounds.

For compound A a 4 Mole excess of alcohol, based on PIB Succinic Anhydride value, was charged to a PIB Succinic Anhydride (PIB maleic anhydride reaction product). The reaction mixture was heated to 190 °C and refluxed until the Acid value was <1 mg NaOH/g. The excess alcohol was then removed.

For compounds B and C, in each case a 1.25 Mole excess of monohydroxy alcohol, based on PIB Succinic Anhydride value, was charged to a PIB Succinic Anhydride (PIB maleic anhydride reaction product). The reaction mixture was heated and refluxed until the Acid value was half the original value. The excess alcohol was then removed. A further 2 Mole excess of polyhydroxy alcohol, based on remaining acid value, was charged and the reaction mixture was heated and refluxed until the acid value was <1 mg NaOH/g. The excess alcohol was then removed.

- A. The PIB was NAPVIS X10 available from BP (mol wt 260, i.e. C<sub>18</sub>), the alcohol was mono ethylene glycol, i.e. this is a comparative compound analogous to compound D of WO97/44507.
- B. The PIB was NAPVIS X10 available from BP, the monohydroxy alcohol was methanol, the polyhydroxy alcohol was mono ethylene glycol. Compound B is in fact a mixture of a methyl / ethylene glycol mixed ester of the PIB succinic acid and the bis ethylene glycol ester of the PIB succinic acid.

- C. The PIB was NAPVIS X10 available from BP, the monohydroxy alcohol was isopropanol, the polyhydroxy alcohol was mono ethylene glycol. Compound C is in fact a mixture of an isopropyl / ethylene glycol mixed ester of the PIB succinic acid and the bis ethylene glycol ester of the PIB succinic acid.

#### Improvement of Fuel Lubricity

A High Frequency Reciprocating Rig (HFRR) bench test, such as described in SAE Technical Paper 932692, can measure the lubricity of base fuels and fuels dosed with lubricity additives. The results of such a test are reported as ball wear in terms of mean wear scar diameter. Lower wear scar diameters are indicative of better lubricity. HFRR wear scar diameter results are compared below for typical North European middle distillate fuels which have been treated with the comparative compound A and with compounds B and C of formula (I). The fuels contain less than 0.05% w/w sulphur content.

	ppm	$\mu\text{m}$
Compound A	75	401
Compound B	100	298
Compound C	88	337
Base fuel	---	622

These results show that the lubricity enhancing effect of the compounds B and C is comparable to compound A, the compound according to WO97/44507.

Interfacial tension

Measurements of differences in surface energies of non-polar solutions and solutions with additives were obtained using a Cahn Dynamic Contact Angle Analyser with Wilhelmy plate and de Nouy ring probes. The analyser comprises an electronic balance, linked to a computer with appropriate software. The force changes on the probe (flame cleaned) passing into or between liquid surfaces are measured as advancing and receding contact angles and thus surface energies can be obtained.

Knowing the dimensions  $p$  of the probe, the contact angle  $q$  and the wetting force  $F$ , recorded by the balance, a modified Young equation

$$\cos q = F/st.p$$

can be used to obtain surface tension  $st$ .

Interfacial tension measurements are given below for the comparative compound A and for compound B of the invention at 100 mg/l in A1 jet fuel, interface with water.

	Dyn/cm <sup>2</sup>
Compound A	4.6
Compound B	23.3

These results show an increased surface tension for the compound B. A higher figure indicates better water separation, one measure of the degree to which additives resist carryover between fuels.

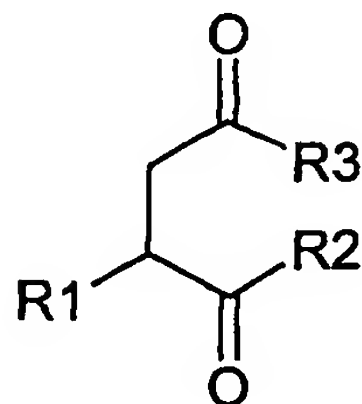
Msep Test

To monitor the effect of additive carryover into jet fuel the Msep test is used. In the Msep test a water/jet fuel sample is emulsified in a syringe with a high speed mixer prior to being expelled through a glass fibre coalescer and the effluent analysed for uncoalesced water by light transmittance. The test monitors the interaction between water and the jet fuel. Normal jet fuel has high (95-100) Msep numbers. Jet fuel containing a static dissipator (eg Stadis450) has a reduced Msep value. To show no harm effects, jet fuel is dosed with 3mg/l additive and the Msep test is carried out. The following Msep test results show the additives have minimal effect on Msep values even at increased levels.

	Concentration mg/l	Msep value
Compound A	3	60
Compound B	3	89, 87
Compound C	3	80

Claims

1. A method of increasing the lubricity of a liquid hydrocarbon fuel comprising the addition of one or more compounds of formula (I)



(I)

where  $R_1$  is a  $C_{10}$ - $C_{150}$  alkenyl group, one of  $R_2$  and  $R_3$  is -OH or the residue of a  $C_{1-20}$  monohydroxy alcohol and the other of  $R_2$  and  $R_3$  is -OH or the residue of either a  $C_{1-20}$  monohydroxy alcohol or a  $C_{1-20}$  polyhydroxy alcohol, with the proviso that  $R_2$  and  $R_3$  are not both -OH.

2. A method as claimed in claim 1 wherein  $R_1$  is a  $C_{16}$ - $C_{80}$  group.

3. A method as claimed in claim 1 or claim 2 wherein  $R_1$  is a polyisobutene

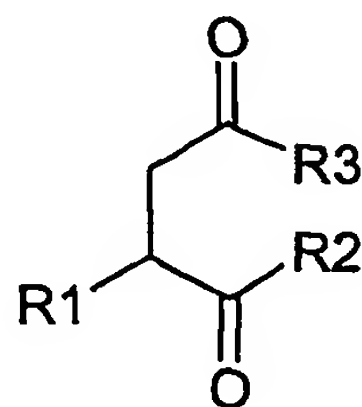
4. A method as claimed in any preceding claim wherein  $R_2$  and/or  $R_3$  are methoxy, ethoxy, n-propoxy or isopropoxy.

5. A method as claimed in any preceding claim wherein one of  $R_2$  and  $R_3$  is the residue of a monohydroxy

alcohol and the other is  $\{-\text{OCH}_2\text{CH}_2\}_n\text{OH}$ ,  $\{-\text{OCH}_2\text{CHCH}_3\}_n\text{OH}$  or  $-\text{OCH}_2\text{CHOHCH}_2\text{OH}$  with  $n = 1-10$ .

6. A method as claimed in claim 5 wherein one of  $R_2$  and  $R_3$  is the residue of a monohydroxy alcohol and the other is the residue of ethylene glycol, diethylene glycol or glycerol.

7. A method as claimed in any preceding claim further comprising the addition of one or more compounds of formula (Ia)



(Ia)

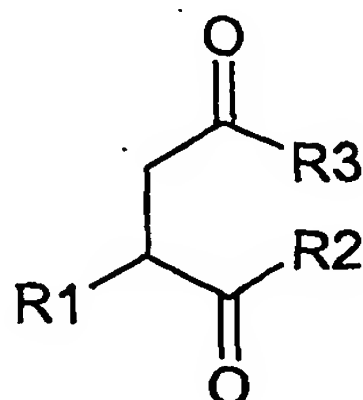
where  $R_1$  is a  $C_{10}-C_{32}$  alkenyl group,  $R_2$  and  $R_3$  are  $\{-\text{OCH}_2\text{CH}_2\}_n\text{OH}$ ,  $\{-\text{OCH}_2\text{CHCH}_3\}_n\text{OH}$  or  $-\text{OCH}_2\text{CHOHCH}_2\text{OH}$  with  $n = 1-10$ , and wherein the compound of formula (I) and the compound of formula (Ia) may be added separately or in combination.

8. A method as claimed in claim 7 wherein  $R_1$  in formula (Ia) is a  $C_{12}-C_{26}$  group.

9. A method as claimed in claim 8 or claim 9 wherein  $R_2$  and  $R_3$  in formula (Ia) are ethylene glycol residues.

10. A fuel composition comprising a liquid hydrocarbon fuel and one or more compounds of formula (I) as defined in any of claims 1 to 6.

11. A fuel composition according to claim 10 further comprising one or more compounds of formula (Ia) as defined in any of claims 7 to 9.
12. A fuel composition according to claim 10 or claim 11 wherein the liquid hydrocarbon fuel comprises a middle distillate fuel, gasoline, kerosine or heavy fuel oil.
13. A fuel additive composition comprising one or more compounds of formula (I) as defined in any of claims 1 to 6, and one or more compounds of formula (Ia) as defined in any of claims 7 to 9, in a fuel-miscible solvent.
14. Compounds of general formula (I)



where  $R_1$  is a  $C_{10}$ - $C_{150}$  alkenyl group, one of  $R_2$  and  $R_3$  is the residue of a  $C_{1-20}$  monohydroxy alcohol and the other of  $R_2$  and  $R_3$  is the residue of either a  $C_{1-20}$  monohydroxy alcohol or a  $C_{1-20}$  polyhydroxy alcohol.

15. Compounds as claimed in claim 14 wherein  $R_1$  is a  $C_{16}$ - $C_{80}$  group.



16. Compounds as claimed in claim 14 or claim 15 wherein  $R_1$  is a polyisobutene

17. Compounds as claimed in any of claims 14 to 16 wherein  $R_2$  and/or  $R_3$  are methoxy, ethoxy, n-propoxy or isopropoxy.

18. Compounds as claimed in any of claims 14 to 17 wherein one of  $R_2$  and  $R_3$  is the residue of a monohydroxy alcohol and the other is  $\{-OCH_2CH_2\}_nOH$ ,  $\{-OCH_2CHCH_3\}_nOH$  or  $-OCH_2CHOHCH_2OH$  with  $n = 1-10$ .

19. Compounds as claimed in claim 18 wherein one of  $R_2$  and  $R_3$  is the residue of a monohydroxy alcohol and the other is the residue of ethylene glycol, diethylene glycol or glycerol.

20. A fuel additive composition comprising one or more compounds of formula (I) as defined in any of claims 14 to 19, in a fuel-miscible solvent.

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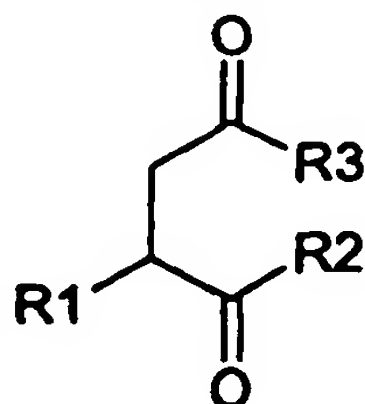
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(54) Title: FUEL ADDITIVES



(I)

(57) Abstract: A method of increasing the lubricity of a liquid hydrocarbon fuel comprising the addition of one or more compounds of formula (I) where R<sub>1</sub> is a C<sub>10</sub>-C<sub>150</sub> alkenyl group, one of R<sub>2</sub> and R<sub>3</sub> is -OH or the residue of a C<sub>1-20</sub> monohydroxy alcohol and the other of R<sub>2</sub> and R<sub>3</sub> is -OH or the residue of either a C<sub>1-20</sub> monohydroxy alcohol or a C<sub>1-20</sub> polyhydroxy alcohol, with the proviso that R<sub>2</sub> and R<sub>3</sub> are not both -OH.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/02975

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10L1/18 C10L10/04 C07C69/593 C07C69/602

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10L C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

BEILSTEIN Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 381 022 A (LE SUEUR WILLIAM M) 30 April 1968 (1968-04-30) examples 2, 18 ---	10, 14-17, 20
X	US 2 993 773 A (STROMBERG VERNER L) 25 July 1961 (1961-07-25) cited in the application the whole document ---	10, 12, 14, 15, 17, 20
X	US 4 255 160 A (PAPPAS PETER G ET AL) 10 March 1981 (1981-03-10) the whole document ---	10, 12, 14, 15, 20
X	US 4 032 304 A (MILLER CLARK OBER ET AL) 28 June 1977 (1977-06-28) the whole document ---	10, 12
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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- \*P\* document published prior to the international filing date but later than the priority date claimed

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\*G\* document member of the same patent family

Date of the actual completion of the international search

26 July 2002

Date of mailing of the international search report

02/08/2002

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## INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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